

Direct Resistless Soft Nanopatterning of Freeform Surfaces

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Supporting Information

ABSTRACT: Nanoimprint is broadly used to pattern thin polymer films on rigid substrates. The resulted patterns can be used either as functional nanostructures or as masks for a pattern transfer. Also, nanoimprint could, in principle, be used for the direct patterning of thermoformable substrates with functional nanostructures; however, the resulted global substrate deformation makes this approach unpractical. Here, we present a new approach for the direct nanoimprint of thermoformable substrates with functional nanostructures through precise maintaining of the substrate shape. Our approach is based on an elastomeric stam soaked



in organic solvent, which diffuses into the imprinted substrate, plasticizes its surface, and thereby allows its imprint at the temperature below its glass transition point. Using this approach, we imprinted features at the 20 nm scale, which are comparable to those demonstrated by conventional nanoimprint techniques. We illustrated the applicability of our approach by producing functional antireflective nanostructures onto flat and curved optical substrates. In both cases, we achieved full pattern transfer and maintained the shape of the imprinted substrates, a combination that has not been demonstrated so far. Our approach substantially expands the capabilities of nanoimprint and paves the way to its numerous applications, which have been impossible by existing nanopatterning technologies.

KEYWORDS: nanoimprint, direct imprint, PDMS, polymers, AR coating

1. INTRODUCTION

Nanoimprint lithography was introduced almost a quarter century ago^{1,2} and since then has revolutionized the world of nanofabrication. Nanoimprint lithography combines (i) nanopatterning with a resolution and minimal feature size down to single nanometers,^{3,4} (ii) scalability and high throughput,^{5,6} and (iii) simple and cost-effective equipment. This unique combination has turned nanoimprint to a preferable approach for device fabrication in numerous applications that include but are not limited to plastic electronics,⁷ photovoltaics,⁸ photonics,9 and biomimetics.10 Nanoimprint can be applied to a variety of thermoplastic and UV-curable resist materials, using either rigid or soft molds.^{11,12} Nanoimprint with soft molds, in turn, allows patterning of nonplanar surfaces,¹³ a challenging task for conventional lithographies such as photolithography or electron-beam lithography. Ever since its invention, nanoimprint lithography has been mostly used to produce resist masks, whose pattern is transferred into the underlying substrate by, for instance, plasma etching or metal deposition and liftoff. However, the ability of nanoimprint 3D relief micro and nano structures, especially in the gray scale,¹⁴ has opened a pathway to the direct patterning of functional materials in many applications, for example, polymer solar cells,¹⁵ organic laser,¹⁶ and organic LEDs.¹⁷

Besides its great advantages, nanoimprint has a fundamental limitation: it can only produce patterns in thin films on rigid (usually inorganic) substrates. If a substrate is made of an organic polymer, its surface can be patterned by applying and imprinting a thin film of UV resist⁵ or of a thermal resist with a glass transition point lower than that of the substrate.¹⁸ In the latter case, the imprinting temperature must be somewhere between the two glass transition points to allow thermal imprinting of the resist and at the same time to prevent the global deformation of the substrate. Notably, applying a film of the resist onto a polymer substrate means that the functional pattern will be imprinted not in the substrate itself but within the layer of a "foreign" material (Figure 1a). Such a restriction, in turn, often complicates the fabrication process and substantially limits the choice of materials for a required functional nanopattern. For instance, an imprinted film must have a strong adhesion to the substrate. Furthermore, both the substrate and film materials must have similar thermal expansion coefficients; otherwise, the film will generate a mechanical stress upon thermal cycle, which may result in cracks and delamination of the film. In optical applications, the refractive index of the imprinted film often must match that of the substrate; otherwise, an unwanted optical interface will be formed.¹⁹ Overall, it would be ideal for many applications to directly pattern the surface of the substrate with functional nanostructures, without applying a foreign material.

Direct patterning of polymer substrates has been demonstrated by hot embossing, yet mostly for features sized in the micron scale and above.²⁰ Chen et al. have recently demonstrated hot embossing of curved substrates using a

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Different expansion coefficients



Figure 1. Various concepts of surface patterning by nanoimprint. (a) Conventional nanoimprint of a thin film of resist on a rigid substrate. (b) Hot embossing at a low temperature at the range of T_g or slightly above, resulting in incomplete pattern transfer. (c) Hot embossing at a temperature substantially higher than $T_{g'}$ resulting in global deformation of the imprinted substrate. (d) Ideal direct imprint in which the pattern is fully transferred and the substrate shape is maintained.



Figure 2. (a) Schematic process flow of the direct imprinting of a polymeric substrate. (b, c) Direct imprinting of nanometric features on the surface a polymeric substrate. The high-magnification SEM, as well as the measured surface profile with the measured FWHM, indicates the achieved minimal feature size.

soft mold.²¹ However, the attempts to reproduce features sized below the micron scale resulted only in partial pattern transfer. Furthermore, to achieve even a partial pattern transfer, a temperature far above the glass transition point of the embossed polymer had to be applied, resulting in a significant thermal expansion of the PDMS mold and, as a consequence, a distortion of up to 15%. Still, the main constrain of hot embossing is the compromise between the pattern quality and maintenance of substrate shape (Figure 1b,c): embossing at a temperature slightly above the glass transition point yields incomplete pattern transfer while embossing at a higher temperature deforms the substrate.²² Such a deformation is often intolerable, especially when the substrate is used as an optical component such as a lens. Again, it would be ideal for many applications to fully transfer the pattern while maintaining the shape of the polymeric substrate (Figure 1d); however, this seems to be fundamentally impossible by conventional hot embossing.

In this paper, we present a new nanofabrication approach that allows to directly nanoimprint the surface of a thermoplastic substrate with full pattern transfer and without deforming the shape of the imprinted substrate. This approach is based on a soft nanoimprint mold made of polydimethylsiloxane (PDMS), which is soaked prior the imprinting in a solvent to be able to dissolve the substrate material (Figure 2a). During the soaking, the mold absorbs the solvent and thereby becomes a solvent reservoir. While the soaked mold is brought in contact with a polymeric substrate, the solvent diffuses from the mold into the polymer surface and absorbs within a thin layer at its surface. This solvent absorption by the polymer surface produces a plasticizing effect by reducing its glass transition point. Thus, while the plasticized surface of the polymer can be imprinted at a temperature below the glass transition point of the raw polymer, the bulk of the substrate will not be affected by the imprint at all. In this paper, we showed that our novel nanoimprint approach allows the direct imprinting of a polymer substrate with features sized at sub-20 nm scale. Such a size scale is close to that of the state-of-the-art thermal nanoimprint of thin films. We also modeled the absorption of the solvent and found that it forms a plasticized surface layer of a few microns. To demonstrate the applied potential of our imprinting approach as well as its ability to precisely reproduce nanostructures with a controlled 3D shape, we directly imprinted subwavelength antireflective moth-eye nanostructures on the surface of an optical polymer and showed that it effectively attenuates its surface reflection. Finally, we demonstrated direct nanoimprint onto a curved polymer surface by imprinting moth-eye antireflective nanostructures onto a polymeric lens of optical glasses. Overall, we demonstrate here a paradigm-shifting advance in soft nanoimprint, a commonly used lithography limited, however, to pattern thin films only, by redefining it as a direct, resistless nanopatterning. This advance, in turn, paves the way to numerous applications that require a facile, scalable, and flexible methodology for the nanopatterning of surface of polymeric substrates with freeform shapes.

2. RESULTS AND DISCUSSION

Important aspects of any nanolithographic technique are its resolution and the minimal feature size. To explore the miniaturization limits of our direct resistless nanoimprint, we produced an elastomeric mold patterned with various shapes whose critical dimension was down to 20 nm. For this purpose, we first fabricated a master by electron-beam patterning of a positive resist on silicon substrates. We then replicated a soft mold from this master by sequential application of hard and soft PDMS²³ (see Supporting Information, Figure S1 for the detailed process description). To directly imprint the polymer substrates, we first soaked the mold in toluene for 5 min and dried it with nitrogen. Immediately after the soaking, we brought the mold into contact with a circular substrate (diameter of 2.54 cm) of an optical cyclo-olefin polymer (Zeonex, Zeon Inc.) and imprinted it with a custom-made nanoimprint tool^{24,25} by applying a pneumatic pressure of 50 psi and a temperature of 100 °C for 10 min. By the end of the imprint process, we brought the substrate and the mold to room temperature by natural cooling, released the pressure, and gently peeled the mold off the substrate.

The glass-transition temperature of the used optical polymer is 138 °C, according to the vendor website. Naturally, imprinting at 100 °C did not change the shape of the polymer substrate (Figure S2). On the other hand, we found that its surface was faithfully imprinted with the desired pattern (Figure 2b,c). After analyzing both the size and the shape of the imprinted nanostructures, we concluded that the resulting nanopattern faithfully replicates the one originally defined by the master, with no detectable pattern distortion. The achieved 20 nm feature size is close to that obtained by the state-of-the art nanoimprint of UV or thermal resist films using soft molds.¹³ The line edge roughness (LER) of the imprinted features, which is notable on high-magnification SEM images, is about 2.2 nm (see the Supporting Information for the calculation). To test whether the obtained LER is not an imaging artifact resulted from the charging and heating of the polymer during SEM inspection, we also measured the LER of imprinted lines with the width of 200 nm (Figure S3) and found it to be \sim 25 nm. In these two cases, the LER value is in proportion with the line width and therefore is likely caused by the patterning process rather than by SEM imaging. To confirm that the applied nanoimprint did not deform the global shape of the imprinted substrate, we characterized its flatness by both laser scanning profiler and profilometry (Figures S4 and S5). We compared the obtained flatness with that of a bare substrate and found that our nanoimprint process did not produce any bow or other types of substrate deformation. This finding is very important, especially for potential optical applications, in which the global shape of imprinted optical components, such as lenses, must be precisely maintained.

PDMS swells upon absorbing organic solvents. Naturally, this swelling can alter the dimensions of the imprinted pattern. To asses such a possible pattern distortion, we first estimated how much toluene is absorbed by the mold after 5 min of soaking. To that end, we measured the weight and volume of PDMS mold before and after the soaking. We found that the mold volume increased by $\sim 10\%$ upon soaking and that the amount of the absorbed toluene was ~ 0.12 g/cm³ of PDMS. Interestingly, we also found that both the degree of swelling and the amount of absorbed toluene decreased by more than half after the imprinting. Obviously, the mold shrank during the imprinting because a great part of toluene diffused out. Naturally, some part of the diffused toluene absorbed at the polymer surface and produced there a plasticizing effect. To estimate the possible pattern distortion due to the mold swelling, we measured the periodicity of an imprinted grid, whose nominal periodicity was 80 nm, as defined by the master

mold. To maximize the precision in the periodicity value, we measured the full width at half-maximum (FWHM) of its grid profile (Figure S6). We found that the periodicity of the imprinted pattern increased uniformly across the pattern to 81.3 nm, which is an increase of 1.17% compared to original 80 nm periodicity in the grating on the master mold. This increase in the grating periodicity is inconsistent with the observed 10% of the mold expansion after the soaking. We believe that during the imprint, most of the absorbed solvent leaves the mold, and thus, the mold volume and therefore its surface goes back to its original dimensions. We also believe that the observed pattern distortion, which is small considering the fact that we used a soft flexible mold, can be further reduced by optimizing the process parameters, such as the amount of absorbed toluene. Notably, we repeated the measurements after a few days and found that the pattern dimensions stay consistent. This verifies that any possible desorption of toluene leftovers in the imprinted polymer does not affect the pattern.

To optimize the direct resistless nanoimprint process and to be able to rationally design its process parameters, the solvent transfer from the mold to the imprinted polymer must be fundamentally understood. Here, we used a basic diffusion model to describe the transfer of toluene from the mold into the imprinted polymer during the imprinting. For this purpose, we assumed that the toluene concentration at the polymermold interface is constant during the imprint and that this concentration is equal to the bulk toluene concentration in the soaked mold. This assumption is used as a boundary condition for the diffusion equation that describes the toluene migration into the polymer (see Supporting Information, Figure S7). Given the diffusion coefficient of toluene in cyclo-olefin polymer of 7.5×10^{-12} cm² s^{-1 26} and neglecting a possible effect of the surface topography created by the mold, we obtained a characteristic diffusion length of 670 nm after 10 min of imprinting. Naturally, the diffusion profile propagates with time, resulting in a toluene-containing layer of a few microns at the polymer surface. It is difficult to quantitatively predict the effect of toluene concentration in the polymer at the polymer glass-transition temperature. Still, our experimental results clearly show that the absorbed toluene effectively plasticized the polymer and allowed its imprinting at a temperature of about 40 degrees below the transition point of the raw polymer. Furthermore, the thickness of the plasticized layer, as predicted by our simplistic model, is a few microns. This confirms that our resistless imprinting approach can be used to produce 3D features with a high aspect ratio and vertical dimensions on the micron scale.

It should be noted that organic solvents were previously used to facilitate imprint of polymers. One example is solventassisted microcontact molding (SAMIM) pioneered by Whitesides and Co.²⁷ Yet, several cardinal differences between SAMIM and our approach must be highlighted. First, in SAMIM, the solvent is directly applied on the interface between PDMS mold and polymer and diffuses into both the polymer and mold in an uncontrollable manner. In our approach, on the contrary, the solvent is first soaked in the mold and only then diffuses into the polymer; thus, the overall solvent amount and, therefore, the diffusion length and the thickness of the imprintable layer, are all highly controlled by the soaking time. Also, we demonstrated here that the minimal feature size must below that was achieved by traditional SAMIM. Finally, and most importantly, SAMIM, as well as other similar solvent-assisted imprint approaches,²⁸ were



Figure 3. Moth-eye antireflective coating on the surface of Zeonex substrate. (a, b) 2D AFM of the used mold and the imprinted polymer, respectively. The insets show the 2D profile to demonstrate that the features have the same height. (c, d) 3D AFM and SEM of the imprinted polymer, respectively. (e) Photographic image of a flower seen through the optical polymeric substrate whose central square was nanoimprinted with antireflective nanostructures. (f) Reflection spectra of bare and imprinted polymer substrates.

developed for patterning polymer films on solid substrates, for example, Si. In this sense, solvent-assisted imprint has no conceptual advantage over the traditional thermal or UV nanoimprint. On the contrary, our approach is aimed at the direct surface patterning of polymer substrate while maintaining the substrate shape. This combination cannot be achieved by any existing nanoimprint technique, and our new imprint approach opens therefore the pathway for many applications unachievable to date.

One important application of nanoimprint lithography, which requires features with heights of hundred nanometers and above, is moth-eye antireflective coating. This type of bioinspired optical nanostructure, which was first discovered on the cornea of nocturnal moth Spodoptera eridania about half a century ago,²⁹ is based on dense arrays of subwavelength nipples that produce a layer with an effective index gradient.^{30,31} Compared to traditional, thin-film-based antireflective coatings, moth-eye antireflective coatings are broadband, omnidirectional, and have low laser damage thresholds and better resistance to thermal shocks. Nanoimprint lithography, which combines high throughput with the ability to pattern subwavelength features, was found to be an ideal approach for the fabrication of moth-eye antireflective coatings for many applications, such as, for instance, solar cells.³² Still, surface patterning of functional materials with a nanoimprinted moth-eye antireflective coating has mostly required pattern transfer from the imprinted resist to the substrate by etching.³³ Yet, in the case of polymeric optical surfaces, the fabrication of moth-eye antireflective coating could be, in principle, greatly simplified by direct nanoimprint. In such a case, there would be no need to cover the polymer substrate with a "stranger" material, whose optical properties are different from those of the substrate and which can complicate the optical design. Such a direct imprinting of antireflective nanostructures, however, has not been demonstrated up to date.

Here, we directly nanoimprinted the surface of an optical polymeric substrate (Zeonex) with a moth-eye antireflective coating. To that end, we first replicated a hybrid h-PDMS/ PDMS mold from a commercial nickel master patterned with moth-eye conical nanostructures (NIL Technology) and then used it for direct imprinting. To carry out the nanoimprint, we first soaked two PDMS molds in toluene, mechanically pressed them against the substrate from both sides using a set of mechanical clamps, and then placed the pressed substratemold sandwich in an oven heated to 80 °C for 10 min. While the depth of the relief features for the PDMS mold we used was 200 nm (Figure 3a), the corresponding height of the imprinted features was found to be equal to 200 nm as well (Figure 3b). Furthermore, we found that the periodicity of the nanoarray was exactly 347 nm for both the mold and the imprint (Figure S8). These two findings clearly show that the pattern was transferred with very high fidelity, mostly due to the fact that the nanoimprint was carried out at a relatively low temperature at which the PDMS mold expansion in minimized. Figure 3 c,d shows 3D AFM and SEM images of the imprinted features, confirming the high quality of the pattern transfer. Again, the global shape of the imprinted substrate was not affected by the imprint process.

The imprinted antireflective nanostructures effectively increase the transmission of the used optical polymer substrate. Here, the used nanoimprint mold was $\sim 1.5 \times 1.5$ cm in size; thus, we imprinted a square in the middle of a Zeonex substrate with a diameter of 2.54 cm. The difference in the optical transmission between the imprinted and nonimprinted areas is clearly seen in the photograph in Figure 3e. To quantify the optical effect of the imprinted antireflective nanostructures, we measured the reflection spectrum of the imprinted Zeonex in the visible range using a spectrophotometer (Cary 5000, Agilent) and compared it to that of a bare substrate (Figure 3f). It can be seen that the directly imprinted moth-eye antireflective nanostructure produced a broadband reduction in the reflection over the visible spectrum. Notably, we used here a commercial master mold designed for a generic material. We believe that a better antireflective performance than that shown here could be achieved by optimizing the design of the antireflective nanoarrays and, specifically, by matching it to the refractive index of Zeonex.

As previously mentioned, the great benefit of using soft nanoimprint molds is in their ability to pattern nonplanar surfaces. To demonstrate that our imprint approach can be applied to nonplanar surfaces, we produced a similar moth-eye antireflective coating onto a commercial lens of optical glasses made of polycarbonate (PC) whose vertical and horizontal radii of curvature were 81 and 27 mm, respectively. Here, we used the similar mechanical setup previously described for Zeonex, which was based on clamps, to imprint the antireflective nanostructures on the convex side of the lens. Notably, the typical glass transition point of polycarbonate is about 150 °C. We presume that a commercial plasticizer was added to the used polycarbonate to facilitate the injection molding of the lens; however, we do not know to what extent it lowered its glass transition point. Still, the lens did not change its global shape at the imprinting temperature of 80 °C, as can be seen in Figure 4a. Again, as our imprinting mold was ~1.5



Figure 4. (a, b) 2D and 3D AFM of nanoimprinted polycarbonate, respectively. (c) Photographic image of a lens with the imprinted antireflective square in the middle. (d) Reflection spectra on bare and imprinted polycarbonate

 $cm \times 1.5$ cm in size, we could not imprint the entire lens but only its central part. This imprinted square region at the mold center is clearly visible in the photography of the lens because it is more transparent than the surrounding areas. Both the microstructural analysis of the imprinted area and its antireflective performance clearly show that the moth-eye antireflective coating can be as effectively imprinted on a curved substrate as on a flat one.

3. CONCLUSIONS

In summary, this paper presents a new direct resistless nanoimprint of polymeric substrates. This novel nanoimprint approach significantly facilitates the surface nanostructuring of polymeric substrates. A great advantage of this approach, at the core of which is thermoforming of polymer plasticized by its solvent, is that it is done at a relatively low temperature compared to conventional nanoimprint. This low temperature not only prevents the substrate from being globally deformed but also minimizes any possible pattern distortion due to the thermal expansion of the used elastomeric mold, as was demonstrated here. Remarkably, we showed here the nanoimprint of two different polymers. We believe that our nanoimprint approach can be virtually applied to any thermoplastic polymer by using an appropriate solvent for each case. The versatility of our approach, as well as its compatibility with numerous polymer materials and with substrates of any arbitrary form, opens the route to numerous applications that require precise and at the same time scalable nanostructuring of polymer surfaces.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.9b13494.

Schematic process flow of PDMS mold fabrication; polymer substrate after direct imprinting; imprinted lines of 200 nm width used for LER calculation; profiler plots of raw and imprinted polymeric substrates; 3D laser microscopy plots of raw and imprinted polymeric substrates; periodicity measurement of an imprinted grid; diffusion profiles of toluene in the imprinted polymer (Zeonex poly cyclo-olefin) at different imprinting times; and periodicity measurement of the imprinted polymer and mold (PDF)

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Notes

The authors declare no competing financial interest.

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